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ABSTRACT
    Sediment erosion threatens coastal infrastructure and natural habitats throughout the coastal United States. Conventional soil amendments, such as lime, Portland cement, and polyacrylamide, are effective for improving soil strength and resistance to erosion, but exopolymers have the potential to improve sediment stability without the environmental risks of caustic or toxic compounds. This paper describes how the erosional resistance of a pure kaolinite clay is enhanced using two exopolymer analogues, guar gum, a neutral polysaccharide, and xanthan gum, an anionic polysaccharide. A cohesive strength meter was used to measure the critical shear stress τ_{oCr} of high water content muds, representative of newly placed, hydraulically pumped sediment fill. Guar gum produces a nine-fold increase in τ_{oCr} due to increases in pore fluid viscosity and hydrogen bonding between biopolymer strands and clay particles. Xanthan gum provides much less improvement because of electrostatic repulsion. Practical applications of exopolymers for erosion control are discussed.

INTRODUCTION
    Currents or flows gradually remove soil particles on sediment surfaces, and this erosion causes much infrastructure and natural habitat damage, especially along the United States coastline. Louisiana is severely afflicted by this problem, losing one acre of land every 24 minutes because of soft wetland sediment (Fischetti 2001) and subsidence. Of bridge failures between 1989 and 2000, 15.51% were caused by scouring of bridge foundations (Wardhana and Hadipriono 2003), and both external and internal erosion can cause failures of river banks, levees, and dams. One common method for rapidly rebuilding wetlands lost through erosion is hydraulic pumping of dredged sediment to recreate the wetlands. However, the high water content muddy fill deposited by hydraulic pumping has low shear strength, and this poor stability makes freshly deposited fill susceptible to erosion, especially before plants become established.

Care must also be used in amending the soil to improve shear strength because of the toxic or caustic nature of many soil stabilizers. Specifically, ASTM standard D 6276 (ASTM 2006) states that calcium hydroxide or calcium oxide must be added to a soil at a concentration that raises soil pH to 12.4, and this pH is far too alkaline for a healthy marsh ecosystem. Many grouts, such as polyacrylamide, are also toxic, and human exposure must be minimized. Given the large scale and environmentally sensitive nature of wetland restoration projects, traditional amendments are too risky to use. Further, any compound used for improving slurry stability must not inhibit or slow vegetation growth, since plants are also effective for increasing sediment stability. Tengbeh (1993) demonstrated that grass roots can provide a five-fold increase in shear strength over a wide range of water contents, and de Baets et al. (2007) showed that plant roots can increase surface erosion resistance as well. This information provides a strong argument for the use of exopolymers to temporally improve sediment stability because they do not put the environment at risk, like other typical soil stabilizers, while plants become established.

Soil environments have large populations of microorganisms. An important product formed by micro-communities of bacteria, or biofilms, is exopolymers, or extracellular polymeric substances (EPS). Microorganisms produce exopolymers to regulate the microenvironment and to protect themselves against predation and drying. Numerous studies have been performed demonstrating the usefulness of exopolymers in the environment. Typically, exopolymers serve to increase the erosional resistance of sediments when present on sediment surfaces (Widdows et al. 2006; Yallop et al. 2000). For example, in intertidal mudflats, a newly-placed sediment's stability was directly correspondent to that sediment's production and quantity of EPS (Widdows et al. 2006). In sand, *Alteromonas atlantica* built a biofilm that immensely increased the critical shear velocity necessary for the start of sand erosion (Dade et al. 1990). Further, sediment EPS has been found to positively correlate with erosional resistance, while humic acids negatively correlate with erosional resistance (Gerbersdorf et al. 2007).

In addition to erosional stability, a few pilot studies have explored the application of exopolymers to soil treatment and improvement. For instance, artificially added EPS dramatically increased the tensile strength of air-dried strips of the common clay minerals kaolinite and montmorillonite (Chenu and Guérif 1991). Also, the addition of xanthan gum significantly increased the shear strength of Leighton Buzzard sand (Çabalar and Çanakci 2005). Another preliminary study by Nugent et al. (2009) demonstrated how the nanoscale interactions between kaolinite and two EPS analogues, guar gum and xanthan gum, changed the kaolinite's liquid limit.

Louisiana State University (LSU) is studying bioengineered sediment stabilization through the use of exopolymer amendments in an effort to find a solution for wetland erosion that will have minimal environmental impact. Because the Lower Mississippi River Basin and the Northern Gulf Coast mostly have cohesive sediments, this is the type of sediment used in this investigation. This paper describes

how the erosional resistance of a pure kaolinite clay is enhanced using two exopolymer analogues, guar gum, a neutral polysaccharide derived from plants, and xanthan gum, a microbially produced anionic polysaccharide. A cohesive strength meter (CSM) is used to measure the critical shear stress τ_{oCr} of high water content muds, representative of newly placed hydraulically pumped dredge fill. Changes in τ_{oCr} are explained in terms of nanoscale chemical and physical interactions between exopolymer strands and clay particles. Methods for practical application of exopolymers for erosion control are then discussed.

MATERIALS AND METHODS

A relatively pure, untreated, kaolinite clay sample purchased from Theile Kaolin Company was used for this study. Particles smaller than 2 μm made up 98 wt.% of the sample. The specific gravity is 2.63, while the average specific surface area measured 20-26 m^2/g (Flick 1989). Kaolinite was chosen to minimize variance caused by the sediment. Although pure mineral kaolinite is not representative of the composition of Louisiana wetland sediment, it provides a good starting point for determining mechanisms of biopolymer and clay interaction. Specifically, pure mineral kaolinite eliminates interference from foreign organic material, and the low cation exchange capacity of kaolinite reduces variance from cations that can significantly change biopolymer and clay interaction (Nugent et al. 2009). However, the interaction mechanisms developed will not be exclusive to kaolinite, which will allow extrapolation to other cohesive soils. Laboratory Grade guar gum was purchased from Fisher Scientific, and NF Grade xanthan gum was purchased from Spectrum Chemical Manufacturing Corporation. These EPS analogs are described below.

Guar Gum

This neutral polysaccharide comes from *Cyamopsis tetragonoloba* seeds (Risica et al. 2005). Guar gum is capable of hydrogen bonding because it possesses many hydroxyl (-OH) groups. Also, it has a neutral charge because it lacks readily ionizable functional groups, such as carboxylic acid (-COOH) groups. It can produce viscous, pseudoplastic aqueous solutions representative of neutral microbial EPS, even though it is derived from plants. Guar gum has a commercial significance because it is readily available and inexpensive. It also has the ability to increase the viscosity of aqueous systems (Whitcomb et al. 1980).

Xanthan Gum

Xanthan gum is an anionic polysaccharide produced by the bacteria *Xanthomonas campestris* (Sutherland 1994). Its anionic charge comes from hydrogen atoms dissociating from carboxylic acid (-COOH) groups to form carboxylate ($-COO^-$) anions. Xanthan gum's hydroxyl (-OH) groups also allow for hydrogen bonding. Xanthan gum is used commercially because just a small amount of it will greatly increase the viscosity of an aqueous system (Hassler and Doherty 1990). An increased shear rate, however, decreases its viscosity because it is pseudoplastic (Milas et al. 1985).

Preparation of Biopolymer and Clay Specimens

The CSM apparatus uses a water jet contained inside a sensor head, and this sensor head is designed to be pressed into sediment surfaces. Thus, the biopolymer and clay muds prepared for the CSM tests had to be prepared in a fashion that provides a consistent, accessible surface for the 63.5 mm (2.5 in.) wide sensor head. Glass beakers (400 ml) filled with 125 ml of mud provided a surface with enough clearance and sufficient sediment depth to prevent the water jet from eroding enough mud to reach the bottom of the beaker. A starting water content of 180% was used for each mud because this amount of water, when mixed with the kaolinite chosen for this test, produces a fluid mud similar in texture to high water content wetland mud.

It is not useful to describe biopolymer concentration in terms of its pore solution concentration because a saturated clay's water content decreases during consolidation and varies in nature. Therefore, the biopolymer mass ratio, or R_{bm}, is used to measure concentration, which is the ratio of dry biopolymer mass to the sediment dry mass. To produce the specimens used for the CSM tests, a 1.5 wt.% guar gum solution and a 1.5 wt.% xanthan gum solution were first made. Although chemical means can be used to produce homogenous biopolymer solutions, physical mixing would be more practical for field purposes. Dry biopolymer powder was slowly added into distilled/deionized (DDI) water that was stirred by a stir bar over several minutes to reduce clumping. An immersion blender was then used to break down biopolymer powder clumps in the solutions to completely homogenize the solutions. Next, predetermined masses of biopolymer solution, dry kaolinite powder, and DDI water were mixed to produce 125 ml specimens with 180% water contents and appropriate R_{bm} values. Nine specimens were made, which included kaolinite without biopolymer, guar gum and kaolinite mixtures with concentrations of 0.005, 0.010, 0.015, and 0.020 R_{bm}, and xanthan gum and kaolinite mixtures with concentrations of 0.005, 0.010, 0.015, and 0.020 R_{bm}. After adding the materials for each specimen, the materials were lightly stirred with a spatula to prevent driving kaolinite powder into the air and to partially mix the mud. Again, the immersion blender was used to make sure the mud was homogenized.

With the specimens fully mixed, each mud was loaded into a beaker by using a spatula to place portions of mud into the center of the beaker, while being careful not to trap any bubbles of air. As the muds were relatively fluid, they flowed outward and formed a reasonably smooth upper surface. Since dredging is normally done during calm weather and wave conditions, freshly deposited slurry will typically have a few days before being exposed to significant erosional events. Thus, the beakers of mud were placed in a refrigerator at 4 °C for 72 hours to let the mud briefly consolidate under its own weight while minimizing the effect of biological degradation. After 72 hours, those refrigerated muds were allowed to warm to room temperature, and any water present on the mud surface was carefully removed with a paper towel. Then, the CSM sensor head was inserted into the mud surface and was used to measure τ_{oCr}, as described in the next section. Figure 1 provides a picture of the sensor head and a schematic of the sensor head inserted into a sediment surface.
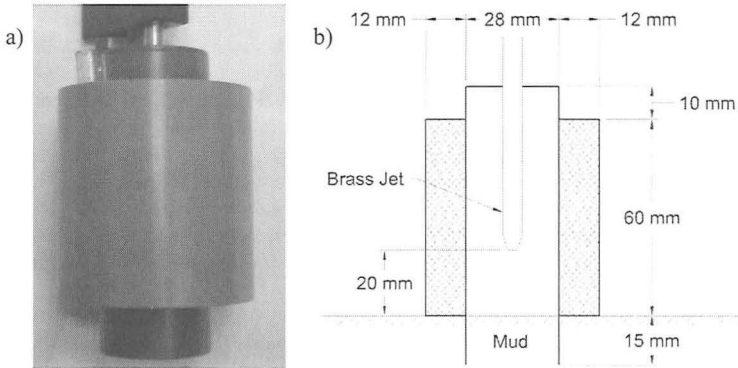
Figure 1. (a) Picture of CSM sensor head and (b) schematic of CSM sensor head cross section inserted into a sediment surface.

Cohesive Strength Meter Methodology and Data Analysis

The apparatus employed was a MKIV 60psi CSM acquired from Partrac Ltd., and it was used based on the guidelines proposed by Tolhurst et al. (1999). With the CSM sensor head in the sediment surface, the sensor head was carefully filled with DDI water, and test program MUD 3 was activated. This test program involves activating the water jet for 0.3 seconds, and then measuring the infrared transmissivity of the water in the sensor head for 30 seconds before activating the jet again. As more sediment is eroded, the transmissivity of the suspension decreases. The jet was initially fired using a driving air pressure of 3.45 kPa (0.5 psi) with the pressure increased by 3.45 kPa (0.5 psi) until a pressure of 34.47 kPa (5 psi) was reached. Afterwards, the pressure was incremented by 6.89 kPa (1 psi) until either a pressure of 413.69 kPa (60 psi) was reached or the operator ended the test early due to the transmissivity approaching 0%. Once the program was complete, some mud around the outside of the sensor head was removed to measure the water content according to ASTM standard D 2216 (ASTM 2006). The sensor head was then removed and cleaned. Because guar gum and xanthan gum are polysaccharides with a high molecular weight, they do not volatilize in the drying oven at 110 ± 5 °C, which means the biopolymer adds to the solid fraction of the water contents and void ratios.

Critical values of shear stress τ_{oCr} for each specimen were determined from the raw CSM data by plotting the transmissivity against time, as shown in Figure 2. Two lines were drawn with the first line going through the linear points before the sediment significantly eroded, and the second line was drawn through the linear points where the sediment is appreciably eroded by the water jet. The intercept is the time where τ_{oCr} is applied to the sediment. As this time is often between jet firings with discrete driving pressures, linear interpolation was used to calculate the intercept jet driving pressure. This driving pressure was then substituted into the equation developed by Tolhurst et al. (1999) to get τ_{oCr}. This equation is used to plot the shear stress curve in Figure 2.
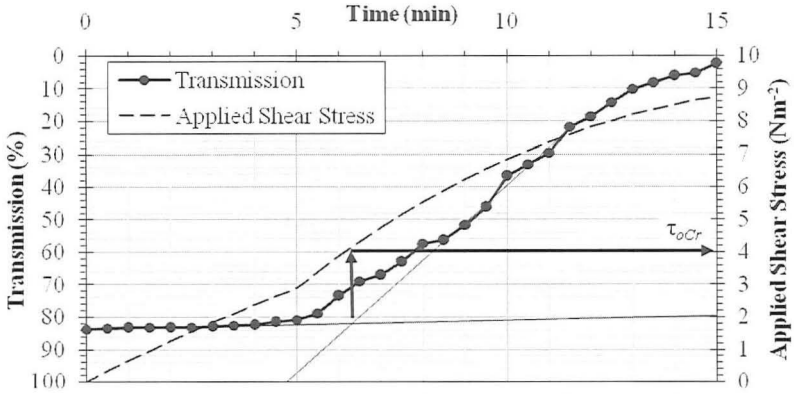
Figure 2. Representative raw CSM data and data analysis.

RESULTS AND DISCUSSION

The results of the guar gum and kaolinite mixture, as well as the results of the xanthan gum and kaolinite mixture are provided in Figure 3. For this figure, the liquid limit values are adapted from Nugent et al. (2009). Except for the 0.015 and 0.020 R_{bm} xanthan gum mixtures, the specimens were able to support the weight of the water filled sensor head needed to successfully complete the CSM tests. The two high concentration xanthan gum mixtures were too fluid to support the water filled sensor head, so valid τ_{oCr} or water content data could not be collected. Erosional resistance for 0.015 and 0.020 R_{bm} guar gum mixtures is increased by a factor of nine over kaolinite on its own, while 0.005 and 0.010 R_{bm} xanthan gum mixtures increase erosional resistance by 1.5 times. Water contents for the tested specimens all fell within 178% ± 4%, which reveals that little consolidation occurred and that the specimens all have approximately the same void ratio.

Figure 3 shows a clear relationship between τ_{oCr} and the liquid limit for guar gum. Nugent et al. (2009) demonstrated that the liquid limit of a guar gum and clay mixture increases as the biopolymer concentration increases because the guar gum boosts the pore fluid viscosity. Since viscosity is a measure of the shear resistance of a fluid, increased pore fluid viscosity leads to greater shear resistance of the overall mixture. In addition, most soils have an undrained shear strength of 1.7-2.0 kPa at the liquid limit (Sharma and Bora 2003), and undrained shear strength is a function of water content (Zentar et al. 2009). Thus, a sediment with a higher liquid limit will generally have a higher undrained shear strength for a given water content. Watts et al. (2003) illustrated a positive correlation between fall cone measured sediment shear strength and τ_{oCr}. As a result, the relationship between τ_{oCr} and the liquid limit is the result of both Casagrande cup and CSM tests indirectly measuring sediment shear strength.

Figure 3 also shows a correlation between τ_{oCr} and the liquid limit for the 0.005 and 0.010 R_{bm} xanthan gum mixtures, although this correlation is muted
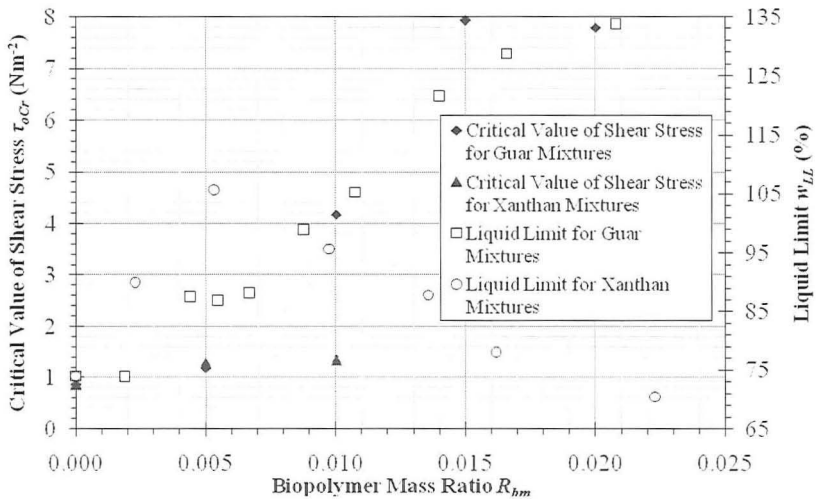
Figure 3. Erosional resistance as a function of biopolymer concentration. Liquid limit values are adapted from Nugent et al. (2009).

compared to the guar gum mixtures. Xanthan gum was also demonstrated by Nugent et al. (2009) to increase the liquid limit by increasing the pore fluid viscosity. However, Nugent et al. (2009) revealed that aggregation caused by xanthan gum at intermediate concentrations reduces the liquid limit to below that of the clay with no biopolymer added. For these intermediate concentrations, the aggregation effect overpowers the pore fluid viscosity effect, while viscosity effects overpower aggregation effects at low and high concentrations. Further, Garrels (1951) demonstrated that the water velocity needed to remove particles from sediment surfaces dramatically decreases as particle size increases for particles smaller than 0.5 mm. The fact that the 0.015 and 0.020 R_{bm} xanthan gum mixtures were too fluid and weak to measure their erosional resistance along with the sediment shear strength and τ_{oCr} correlation provided by Watts et al. (2003) shows that these higher concentration xanthan gum mixtures have a significantly reduced erosional resistance. All together, this suggests that biopolymer induced aggregation negatively affects erosional resistance in xanthan gum mixtures with concentrations greater than 0.010 R_{bm}.

Nugent et al. (2009) also noted that nanoscale interaction between biopolymer strands and clay particles serves to change the liquid limit. Specifically, they found that at biopolymer concentrations with similar pore fluid viscosities, guar gum raises the liquid limit much higher than xanthan gum. This was explained as a result of the guar gum and kaolinite forming an extensive hydrogen bonding network. Xanthan gum and kaolinite interacted little since xanthan gum's negative charge and the overall negative charge kaolinite particles possess at solution pH greater than 2.35 (Alkan et al. 2005) caused electrostatic repulsion that minimized any bonding. A similar effect is demonstrated by the CSM results. Both the 0.020 R_{bm} guar gum

mixture and the 0.005 R_{bm} xanthan gum mixture have zero shear rate pore fluid viscosities of about 30 Pa·s (Whitcomb et al. 1980; Milas et al. 1985). However, the 0.020 R_{bm} guar gum mixture has a τ_{oCr} six times greater than the 0.005 R_{bm} xanthan gum mixture. This disparity is the result of the guar gum and kaolinite forming a hydrogen bonding network, while the xanthan gum and kaolinite electrostatically repel each other.

PRACTICAL APPLICATION

Guar gum and xanthan gum that are added to hydraulically pumped dredged sediment can improve resistance to erosion in wetlands, while minimizing environmental damage. Their non-toxicity also allows plant growth that greatly stabilizes the soil. The biopolymer can easily be added to the sediment through a hydraulic dredge's slurry pump, where it can be completely mixed with the sediment by the slurry output pipe's turbulence. This study demonstrates that the addition of guar gum to newly placed slurry can substantially reduce wetland erosion because guar gum can raise erosional resistance by almost one order of magnitude.

Although xanthan gum provides improvement to the soil, the results of this study showed it to be much less than what was provided by guar gum because of its electrostatic repulsion. This may be misleading. In this study, xanthan gum's negative charge could not be balanced by other cations because DDI water is basically cation free and kaolinite has a low cation exchange capacity. However, calcium ions can form cross-links between xanthan gum strands, greatly increasing the mixture's liquid limit (Nugent et al. 2009). Since there is a relationship between liquid limits and erosional resistance, divalent cations could form ionic bridges and improve erosional resistance through cross-linking. Further, monovalent cations in natural sediment should balance xanthan gum's negative charges, allowing it to form hydrogen bonds. Also note that the pore fluid viscosity, aggregation, hydrogen bonding, and electrostatic repulsion mechanisms described are not interactions exclusive to kaolinite. For example, Ma and Pawlik (2007) found that guar gum forms hydrogen bonds with many minerals, including kaolinite. Therefore, it is possible to extrapolate the results for kaolinite to other clays. However, more study is needed to fully characterize these interactions across a broad range of biopolymers and sediments.

CONCLUSIONS

This study involved performing CSM tests on a kaolinite clay mixed with differing amounts of biopolymer to see how the interaction of these materials would affect its resistance to erosion. Two polysaccharides, similar to natural soil EPS, were used. The polysaccharides included the neutral, plant derived guar gum and the anionic bacterial exopolymer xanthan gum. The following conclusions can be made from the results of the tests:

- As Casagrande cup and CSM tests both indirectly measure shear strength, the results of both tests are linked.
- Increasing biopolymer concentration increases the pore fluid viscosity, and this leads to increased erosional resistance.

- Biopolymer induced aggregation negatively effects erosional resistance.
- For a given pore fluid viscosity, guar gum produces substantially more erosional resistance than xanthan gum since guar gum establishes a hydrogen bonding network between guar gum strands and kaolinite particles.

ACKNOWLEDGEMENTS

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